A Theoretical Model for the True Hardness Determination of Ni-P / SiC Electroplated Composites

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In this work we have applied a Hays –Kendall mathematical model to the Vickers microhardness values to eliminate the troublesome indentation size effect (load dependence of hardness) and obtain a unique value representing the true hardness for each coating. Examination of the unique hardness values has been possible in conditions of heat treatment at 190 ^{0}C and 420 ^{0}C.

Key words: Hays –Kendall model, Ni-P/SiC coatings, hardness, ISE effect, heat treatment

The hardness of Ni-P alloy increases by reinforcing of the Ni matrix with SiC particles. Another possibility for a hardness increase is obtained by applying heat treatments to the Ni-P/Si-C composites coatings [1, 2]. Due to the small thickness of the coatings ranging from 24 to 38 μm very small loads in the range 15-300g have been applied on the indenter when the Vickers microhardness was measured. Such small loads have been selected for producing penetration depths small enough to avoid any influence from the mild steel support on which the coatings were electroplated.

Unfortunately at low loads applied on the indenter the ISE effect (indentation size effect) was manifested that made the measured Vickers hardness H_V to be dependent on the applied load F. In this study we have tried to obtain a unique true hardness value for each coating by making recourse to a theoretical model that tries to disclose the physical reasons for the ISE effect and to propose a mathematical treatment of the experimental hardness data.

The ISE effect and theoretical modalities to eliminate it

Indentation microhardness measurements appropriate for thin coatings can be made by means of various diamond indenters. The most commonly used is the Vickers square pyramid indenter with apex angle 136^o and the Knoop elongated pyramid indenter. Indentation hardness tests have become microhardness tests in 1940 when Hanneman and Bernhardt [3-5] have introduced a Vickers pyramid indenter of very small size (base square diagonal equal to 0.8 mm) in the objective lens of an optical microscope equipped with a device to apply the loads and with a micronic scale for measuring the diagonal of the indentation.

If the geometry of the indenter is taken into account the Vickers microhardness H_V defined as the ratio between the load F and the area of the indentation is expressed as follows:

$$H_V = 2\sin(136^o/2)(F/d^2) = 1854.4F/d^2 \qquad (1)$$

where:

H_V is expressed, kg/mm^2;

F in grams and d in micrometers.

Because the hardness H_V is constant for a given material a direct proportionality between the load F and the size of the indentation d^2 results from (1):

$$F = Kd^2 \qquad (2)$$

Relationship (2) is the well known Kick law and an implicit supposition involved in it is the constancy of the hardness measured at various loads applied on the indenter.

However at low values of the applied load, the Kick law is no more observed and the measured hardness begins to be dependent on the load (see the results we have obtained in table 1). Because the material should have a unique value for its hardness the reason for this troublesome ISE effect has to be looked for in the mechanism of the permanent plastic deformation during the indentation process.

In another work [6] the researches have ascertained the theoretical model proposed by Hays and Kendall [7] to offer a reasonable explanation for the phenomenal occurring during the indentation process and at the same time to offer a possibility to eliminate the ISE effect and to derive the true hardness of the material.

The Hays-Kendall model states that the Kick law would be obeyed at whatever load if one admits the following peculiarity of the indentation process. The force F_2 that effectively produces the plastic deformation during the indentation process is smaller than the applied force F by an amount W. Hence the Kick law should be written as follows:

$$F_2 = F - W = Kd^2 \qquad (3)$$

where W is the force required to initiate the plastic deformation in the material.

By rearranging the terms in eq. (4):

$$F = W + Kd^2 \qquad (4)$$

The physical meaning of (4) is that: for a material having a true hardness H_V the quadratic dependence between the applied load F and the size of the indentation would be obeyed irrespective of the applied load only if a free term W is introduced in the Kick law. A regression statistical treatment applied to the pairs of values F and d^2 experimentally obtained for a given material at various values of the applied load F enables one to calculate the two constants W and K in (4). Constant K is further used to calculate the true hardness of the material by combining (3) and (1). When these equations are used it is important to mention that one has to introduce the effective force F_2 instead of the applied force F, thus obtaining: $F_2 = Kd^2$ for (3) and $F_2 = H_V d^2 /1854.4$ for (1).

By combining these equations can be obtained the true hardness:

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Table 1
RESULTS ON MICROHARDNESS (H_V) MEASURED AT VARIOUS LOADS F FOR ALL INVESTIGATED SAMPLES

Sample ↓	Treatment ↓	F, [g] →	15	25	50	100	200	300
P0S40	None; t=33μm	H_V	210	205,5	203	201,1	200	198,2
		d^2	132,5	225,5	456,7	922	1854,1	2806,6
	190° C; t=36 μm	H_V	254,5	245	242,5	241	237,5	223
		d^2	109,3	189,2	382,3	769,5	1561,6	2494,7
	420° C; t=36 μm	H_V	347	354	303	274	261,5	258
		d^2	80,2	131	306	677	1418,3	2156,3
P5S40	None; t=36μm	H_V	469	473	470	468	454	402
		d^2	59,3	98	197,3	396,2	816,9	1383,9
	190° C; t=38 μm	H_V	649,5	648,5	571	557	518,5	482,5
		d^2	42,8	71,5	162,4	332,9	715,3	1153
	420° C; t=38 μm	H_V	841,5	813,5	803	763	692	643
		d^2	33	57	115,5	243	536	865,2
P10S40	None; t=21μm	H_V	435	429	418	412	407	391
		d^2	64	108,1	221,8	450,1	911,2	1442,8
	190° C; t=24 μm	H_V	537	536	537	501,5	445,5	389,5
		d^2	51,8	86,5	172,7	369,8	832,5	1428,3
	420° C; t=24 μm	H_V	1136	1132,5	1072	1053	951,5	856
		d^2	24,5	40,9	86,5	176,1	389,8	649,9
P20S40	None; t=24μm	H_V	449	437	429	418	404	400
		d^2	62	106,1	216,1	443,6	918	1390,8
	190° C; t=27 μm	H_V	599	545	549	513	453	397
		d^2	46,4	85,1	168,9	361,5	818,7	1401,3
	420° C; t=27 μm	H_V	1159	1114	1107	1002	927	763
		d^2	24	41,6	83,8	185,1	400	729,1

$$H_V = 1854.4\,K \qquad (5)$$

where K is the slope of the straight line obtained by applying the regression statistical treatment to all experimental pairs of values F and d^2.

When the Hays-Kendall model is applied to the experimental hardness measurements performed on thin coatings it is important to make sure that the experimental data are not affected by the hardness of the underneath support. Hence only the data obtained at penetration depths for which the indenter is still in the coating thickness and has not penetrated in the support material will be taken into consideration. If the geometry of the indenter is taken into account the size *d* of the diagonal of the indentation is correlated with the depth of penetration *h*, as follows:

$$h=(d/2)\,tg\,(90^o - 136^o/2) = 0.187d \text{ or roughly } h \sim 0.2\,d \qquad (6)$$

Experimental part

In [2] Vickers microhardness measurements have been carried out for four Ni-P/SiC coatings in three conditions (as plated; heat treated at 190°C for dehydrogenation; heat treated at 420°C for of precipitation hardening).The investigated coatings were denoted as the follows:

P0S40-(0); P5S40-(8.4); P10S40-(16.1); P20S40-(20).

were x in the symbol P_xS_y – (z) indicates the amount of H_3PO_3 in solution in the electrolyte (g/L);

y is the amount of SiC powder in suspension in the electrolyte (g/L) from which SiC particles are co-deposited in the coating during the electroplating process and z is the resulting phosphorus content in the coating (at.%P). If needed an additional index t (representing the thickness of the coating) is introduced in the symbol P_xS_y–(z)-t.

A Shimadzu HMV-2 Vickers microhardness tester was used. The load F was applied perpendicular on the smooth free surface of the coating and a series of loads were applied for each sample as follows: F= 15; 25; 50; 100; 200; 300g. The H_V value was taken as the average of five indentations for each sample.

Results and discussion

Table 1 summarizes the experimental data obtained by the Vickers microhardness test for all investigated samples (measured H_V as well as derived d^2 values). The heat treatment applied and the coating thickness t were indicated in column 2 for each sample. By comparing the values for the coating thickness t with the penetration depth h (calculated by means of (6)) it appears obvious that no influence from the underneath support material (the mild steel) was exerted on the hardness of all investigated Ni-P/SiC coatings, for forces F applied on the indenter below 300 g. Examination of the hardness values in Table 1 shows that the hardness measured for a given sample has not a unique value but is dependent on the applied load F (the ISE effect).

The data from table 1 were further processed by a regression statistical treatment according to the Hays-Kendall model expressed by (5). The straight line obtained for each sample is presented in the series of graphical representations in figure 1-12. The resulting W and K values as well as the confidence factor r^2 for each coating are given in table 2 together with the true hardness calculated by means of (5) according to the Hays-Kendall theoretical model.

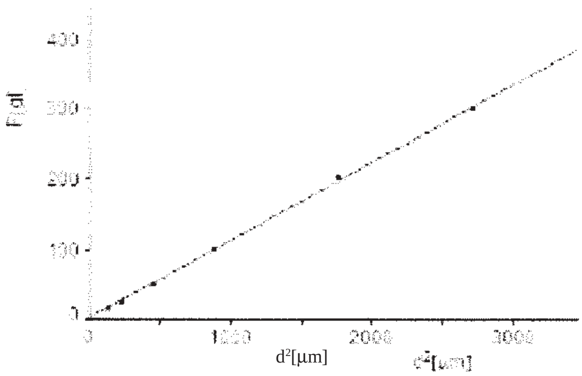

Fig. 1. POS40 non-heat treated

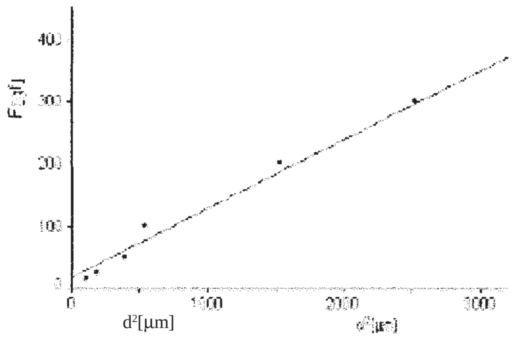

Fig.2. P0S40 heat treated at 190˚C

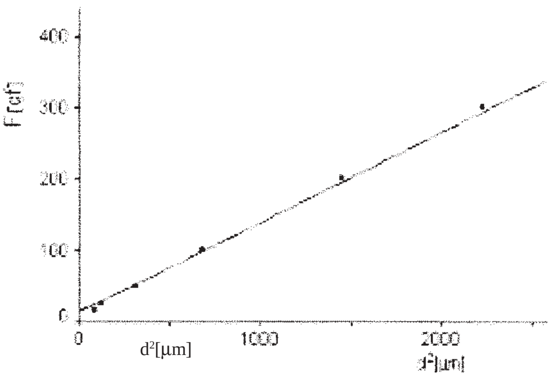

Fig.3. P0S40 heat treated at 420ºC

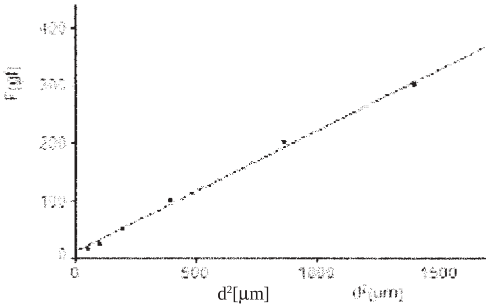

Fig. 4. P5S40 non-heat treated

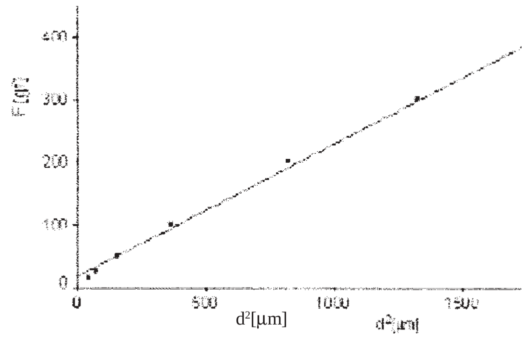

Fig.5. P5S40 heat treated at 190ºC

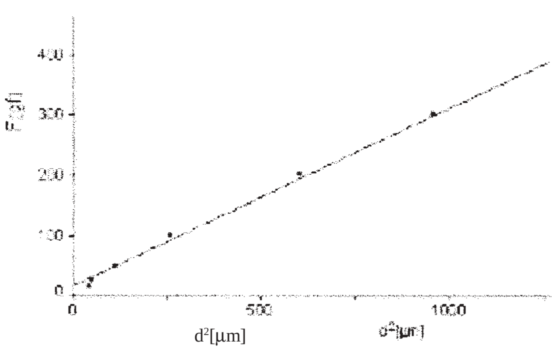

Fig.6. P5S40 heat treated at 420ºC

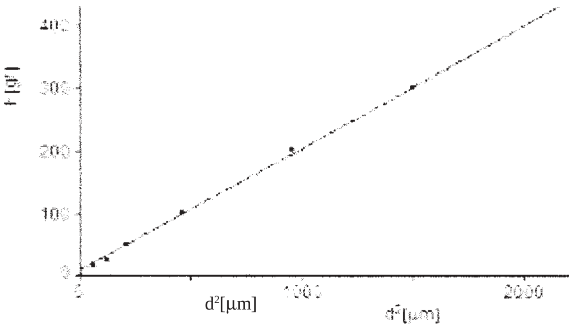

Fig.7. P10S40 non-heat treated

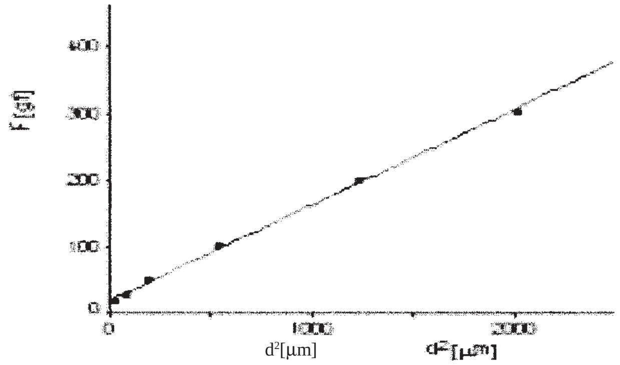

Fig.8. P10S40 heat treated at 190ºC

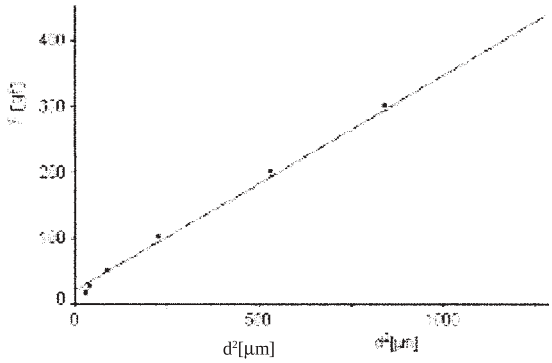

Fig.9. P10S40 heat treated at 420˚oC

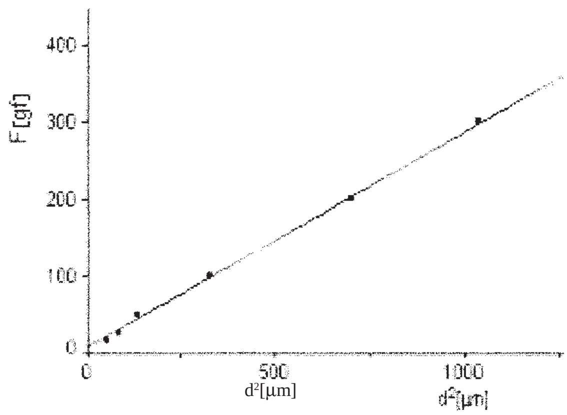

Fig.10. P20S40 non-heat treated

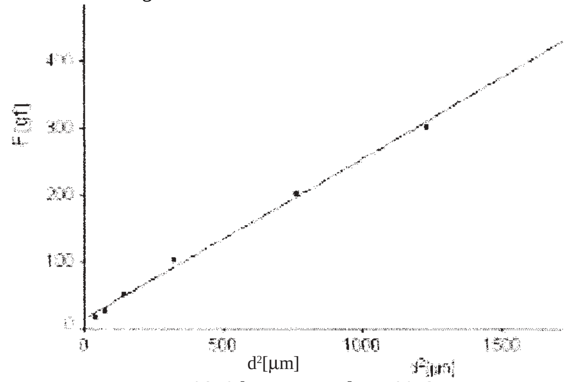

Fig.11. P20S40 heat treated at 190ºC

Table 2

TRUE HARDNESS OF THE INVESTIGATED NI-P/SIC COMPOSITE COATINGS OBTAINED BY THE HAYS-KENDALL THEORETICAL MODEL APPLIED TO THE EXPERIMENTAL HARDNESS DATA

Sample	Heat treatement	r^2	W	K	HV [kgf/mm^2]
P0S40	none	0,999972	1,2258	0.1067	198
P0S40	190° C	0,998434	4,3291	0.1206	224
P0 S40	420° C	0,999827	6,7021	0.1363	253
P5 S40	none	0,994155	7,7874	0.2179	404
P5 S40	190° C	0,997813	8,5885	0.2577	478
P5 S40	420° C	0,997104	9,2536	0.3403	631
P10 S40	none	0,998880	4,0437	0.2082	386
P10 S40	190° C	0,992047	13,0296	0.2080	386
P10 S40	420° C	0,994873	10,5598	0.4582	850
P20 S40	none	0,999882	3,0712	0.2141	397
P20 S40	190° C	0,992370	13,3584	0.2116	392
P20 S40	420° C	0,986495	15,9282	0.4086	758

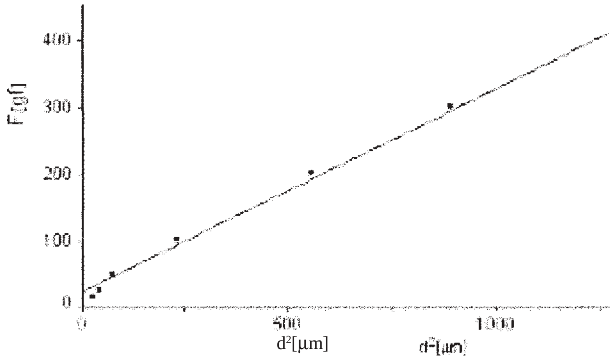

Fig.12. P20S40 heat treated at 420°C

The data in table 2 points to a confidence factor r^2 when applying the regression statistical treatment to the experimental values F and d^2 according to the Hays-Kendall model that was better than 0,99 for 11 among the 12 investigated samples. This good compliancy proves the Hays-Kendall model to be appropriate for eliminating the ISE effect for thin coatings.

Concerning the true hardness values H_v derived from the experimental data by applying the Hays-Kendall model it is interesting to compare the lowest value in table 2 with the highest one. The lowest value H_v = 198 kg/mm^2 belongs to the as plated composite coating containing no phosphorus in its Ni metallic matrix. Its hardness is twice the value reported in [8] for pure Ni that is 110 kg/mm^2 and this increase in hardness has to be ascribed to the reinforcing micronic SiC particles dispersed in the Ni matrix of the coating. Taking this lowest value H_v =198 as a reference the true hardness values in table 2 show the possibility of an increase of the coating hardness as large as 4 times by introducing P in its Ni metallic matrix during the electroplating process and further on by an efficient handling of this phosphorus through a precipitation hardening heat treatment that takes P out of the Ni based solid solution and redistributes it as finely dispersed Ni_3P particles.

Conclusion

On the other side as the agreement between a theoretical model and the experimental data may also depend on the accuracy of the latter ones, one may ascribe the lower values for the confidence factor r^2 in some instances to a poorer quality of the measured values.

Though parameters W and K are independent and result merely by the mathematical treatment of the measured experimental values F and d^2 one may see in table 2 an increase in W as the true hardness H_v increases. As H_v was calculated in the Hays-Kendall model by multiplying factor K by a constant, the correlation between W and H_v has a physical meaning in the framework of the mechanism of initiating the plastic deformation in the process of indentation.

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